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*Published in:*  
Chemical Engineering Science

*DOI:*  
[10.1016/0009-2509\(92\)87155-J](https://doi.org/10.1016/0009-2509(92)87155-J)

**IMPORTANT NOTE: You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.**

*Document Version*  
Publisher's PDF, also known as Version of record

*Publication date:*  
1992

[Link to publication in University of Groningen/UMCG research database](#)

*Citation for published version (APA):*

Veldsink, J. W., Damme, R. M. J. V., Versteeg, G. F., & Swaaij, W. P. M. V. (1992). A catalytically active membrane reactor for fast, exothermic, heterogeneously catalysed reactions. *Chemical Engineering Science*, 47(9), 2939-2944. [https://doi.org/10.1016/0009-2509\(92\)87155-J](https://doi.org/10.1016/0009-2509(92)87155-J)

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## A catalytically active membrane reactor for fast, exothermic, heterogeneously catalysed reactions

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### Abstract

A membrane reactor with separated feed of reactants is demonstrated as a promising contactor type when dealing with heterogeneously catalysed, very fast and exothermic gas phase reactions. Due to the separation of reactants a good control of the system is obtained, because process variables can be varied independently from each other. Transport of reactants is the rate governing process and because this is only slightly temperature dependent a thermal runaway will not occur. When dealing with e.g. combustion processes no explosive mixtures will build up and safety is increased. Based on the dusty-gas model, the concentration profiles of components inside the membrane can be calculated together with the fluxes. However this is a calculation time consuming process and not necessary in all cases. In absence of a pressure drop and no slip of reactants to the opposite side a linearisation is possible leading to a simplified expression for the interfacial flux of a reactant and a criterion to evaluate the possibility of slip of reactants. Using the oxidation of carbon monoxide catalysed by platinum as a model reaction this approximation was experimentally verified by comparison of measured fluxes with the calculated results. Apart from flux measurements exploratory overall conversion measurements were carried out with the membrane reactor module in order to demonstrate its operation performance. From these studies it was concluded that conversion levels up to 90% carbon monoxide could easily be achieved.

### 1. Introduction

Recently in our laboratory a catalytically active membrane reactor with separated feed of reactants was studied by Slood with an extremely fast reversible reaction (Slood et al., 1990). In this reactor the reactants were separated by a catalytically active membrane and owing to transport in the pores inside the membrane reaction proceeds. On studying the well-known Claus reaction, this principle was demonstrated to be very useful when dealing with reactions requiring strict stoichiometric feed of reactants. From numerical simulations Slood showed that applying a pressure difference over the membrane, favours the fluxes while the products can be directed preferentially to one side of the membrane. Zaspalis (1991a, 1991b) also used a catalytically active membrane in the NO<sub>x</sub>-reduction and methanol dehydrogenation reactions. He discussed different types of operation (e.g. premixed and separated feed) with respect to the influence on selectivity.

Separated feed of reactants to the reactor offers advantages with respect to safety in case mixing of reactants is restricted to explosion boundaries. A second advantage is an improved controllability, because all process variables can be varied independently from each other. As the rate governing process is the transport of reactants, thermal runaway will not occur when dealing with exothermal reactions, so if the heat can be removed from the membrane surface, this type of reactor offers a suitable alternative when dealing with very fast, exothermic, heterogeneously catalysed gas reactions. Zaspalis and Slood did not take any heat effects into account as these effects were small.

In the present study an attempt was made to develop a membrane reactor suited for the handling of more concentrated feedstocks and exothermic reactions. In order to be able to predict the fluxes through the membrane a mathematical flux model was developed based on the elaborate Dusty-Gas-Model (Mason & Malinauskas, 1983) and is treated in the first part of this study. Furthermore an approximate model is suggested, saving a lot of computational time and this model is compared to the extended numerical model. In the second part a pilot plant study of the oxidation of carbon monoxide over a membrane, impregnated with platinum will be described. The experimental results will be discussed with respect to the theoretical analysis, given in the first part.

### 2. Dusty Gas Model

Fluxes can be obtained by solving the instationary differential mass balance over a slab of membrane, reading:

$$\frac{\varepsilon}{RT} \frac{\partial P_i}{\partial t} = - \frac{\partial N_i}{\partial z} + R_i \quad (\text{mol.m}^{-3}\text{cat.s}^{-1}) \quad (1)$$

Initial and boundary conditions are e.g. (Dirichlet type):

$t=0:$	$P_i(0,z) = P_i(z)$	$\forall z, i = 1..n$
$z=0:$	$P_i(t,0) = P_i(0)$	$\forall t, i = 1..n$
$z=1:$	$P_i(t,1) = P_i(0)$	$\forall t, i = 1..n$

$R_i$  represents a kinetic rate expression and is in general some explicitly known function of the partial pressures and the temperature. For the inert species this function equals zero, so:

$$R_i = f(T, p_1, \dots) \text{ and } R_{\text{inert}} = 0 \quad (\text{mol.m}^{-3}\text{cat.s}^{-1}) \quad (2)$$

In view of the open structure of the membrane, the gas transport inside the membrane is modelled according to the Dusty-Gas-Model (Mason & Malinauskas, 1983; Krishna, 1987). According to the DGM, the flux of component  $i$  can be expressed as:

$$\sum_{j=1, j \neq i}^n \frac{x_j N_j - x_i N_i}{PD_{ij}^e} - \frac{N_i}{PD_{i,k}^e} = \frac{1}{RT} \frac{dx_i}{dz} + \frac{x_i}{PRT} \left( \frac{B_0 P}{\mu D_{i,k}^e} + 1 \right) \frac{dP}{dz} \quad (i = 1..n) \quad (3)$$

The diffusion coefficients are effective parameters and depend on the structure of the porous medium:

$$D_{i,k}^e = \frac{4K_0}{3} \sqrt{\frac{8RT}{\pi M_i}} \quad D_{ij}^e = \frac{\varepsilon D_{ij}^e}{\tau}$$

The membrane structure is taken into account by the structure parameters  $K_0$ ,  $B_0$  and  $\varepsilon/\tau$ , which can be determined experimentally and independently (Mason & Malinauskas, 1983). The model is completed by the equation:

$$\sum_{i=1}^n x_i = 1 \quad (5)$$

The model was numerically solved on a DEC 5000/200 system, by a finite difference technique (Baker & Oliphant, 1960). Because of non-linearity the remaining set of fully implicit algebraic equations should be solved by iteration, using a Newton method, described in more detail by Press *et al.* (1987) and Sloot *et al.* (1990). The model as expressed in eq. (1) to (5) allows for the calculation of the concentration profiles over a membrane and yields fluxes of the various components as a function of kinetics, transport parameters, boundary conditions and so on. Many simulations have been done in order to study the influence of one of these parameters on the performance of a catalytic membrane. For the purpose of the present study however the calculations were largely restricted to situations where pressure differences were absent and the number of molecules in the gas phase did not change during reaction.

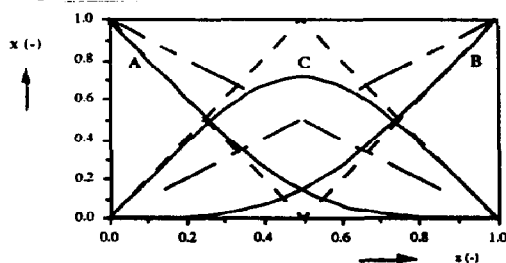


Fig. 1: Dimensionless profiles over the membrane of reactants and product for the reaction  $A + B = 2C$ . The figure shows profiles at different values of the rate constant, (mol.Pa<sup>-1</sup>.m<sup>-1</sup>.s<sup>-1</sup>)

—  $k_{1,1} = 0$  —  $k_{1,1} = 1 \cdot 10^{-7}$  —  $k_{1,1} = 0.1$

Table 1: Model parameters

$D_{i,k}^e = 28.2 \cdot 10^{-6}$ (m <sup>2</sup> .s <sup>-1</sup> )
$D_{ij}^e = 10.5 \cdot 10^{-6}$ (m <sup>2</sup> .s <sup>-1</sup> )
$r_p = 5.0 \cdot 10^{-7}$ (m)
$L = 2 \cdot 10^{-3}$ (m)

Table 2: Structure parameters of the membrane

$B_0 = 7.86 \cdot 10^{-16}$ (m <sup>2</sup> )
$K_0 = 9.96 \cdot 10^{-9}$ (m)
$\bar{r}_p = 317 \cdot 10^{-9}$ (m)
$\varepsilon/\tau = 0.081$
$\phi = 0.31$

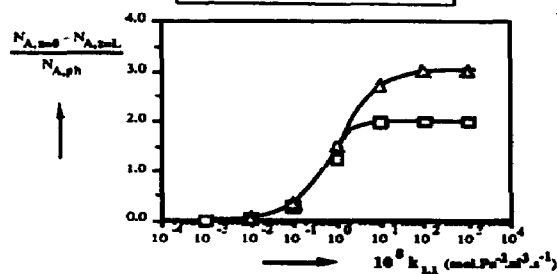


Fig. 2: Relative net flux of A converted in the membrane as a function of the rate constant for a reaction scheme  $A + B = 2C$  (□) and  $A + 0.5B = C + 0.5D$  (Δ)

In case a pressure difference over the membrane is absent and the total number of molecules remains constant, the viscous flow does not contribute to the total flux (no pressure gradients) and the remaining transport mechanism of importance is molecular diffusion of components. As an example of this situation calculations were done for the reaction scheme  $A + B = 2C$  with (1,1)-order kinetics,  $R_A = -k_{1,1}(T)p_A p_B$  (see (2)) and model parameters as given in Table 1. For various values of the rate constant the dimensionless profiles of A, B and C over the membrane are shown in Fig. 1 and Fig. 2 plots the net relative flux of A consumed, defined as the flux of A at the interface  $z=0$  ( $N_{A,z=0}$ ) minus the slip flux ( $N_{A,z=L}$ ), divided by the maximum physical flux ( $k_{1,1}=0$ ), against the value of the rate constant. Besides the reaction scheme  $A + B = 2C$  also the results for  $A + 0.5B = C + 0.5D$  are plotted in Fig. 2. This net relative flux consumed reaches a maximum value, depending on the reaction scheme. A similar phenomenon is commonly known in the theory of mass transfer with chemical reaction in a stagnant liquid film as maximum enhancement (see e.g. Westerterp *et al.*, 1983). From the results of the simulations it was concluded that this maximum value was reached as soon as the slip flux of A to the opposite side ( $N_{A,z=L}$ ) became negligible.

By means of the present mathematical model based on the DGM it is possible to calculate concentration profiles over the membrane and obtaining fluxes from these concentration profiles. From Fig. 2 it can be concluded that a minimum value of the rate constant exist above which no slip of reactants to the opposite membrane side occurs. In this case the flux of a reactant at the membrane interface can be easily calculated as the maximum physical flux multiplied by some maximum enhancement factor, which depends on the reaction stoichiometry, similar to the theory of enhanced gas-liquid reactions. From many calculations for various reaction schemes it was also concluded that this maximum value was reached as soon as the slip flux became negligible, i.e. all reactants are consumed in the membrane. In this regime the membrane reactor with separated feed of reactants exposes its attractive features, so much calculation time and effort could probably be saved, if a criterion could be given expressing the slip in terms of the rate constant and transport properties. Once this criterion is matched the flux of the reactants is easily calculated as was concluded from Fig. 2.

### 3. Approximate model

Assuming that the effect of drift fluxes is of only minor importance, a 'Fickian' expression results, extended with a viscous flow contribution:

$$N_i = \frac{\bar{D}_i^e}{RT} \left( P \frac{dx_i}{dz} + x_i \left[ \frac{B_0 P}{\mu D_{i,k}^e} + 1 \right] \frac{dP}{dz} \right) \quad \text{with} \quad \frac{1}{\bar{D}_i^e} = \left( \frac{1}{D_{i,k}^e} + \sum_{j=1, j \neq i}^n \frac{x_j}{D_{ij}^e} \right) \quad (6)$$

The approximation will be reasonable in the absence of a pressure difference or when dealing with small pressure differences or very small pore diameters, mathematically formulated as  $B_0 P / \mu D_{i,k}^e \ll 1$ . As argued in the preceding paragraph the key parameter is the flux of a reactant at both the membrane interfaces. With respect to component A the flux at  $z=0$  (A-side) then expresses the consumption of A as soon as the flux of A at  $z=1$  (B-side, slip,  $N_{A,z=1}$ ) has become negligible. Substitution of (6) in the stationary mass balance (1) of components A and B in absence of a pressure drop and (1,1)-order kinetics results in differential equations:

$$\frac{dN_A}{dz} + k_{1,1} P_A P_B = 0 \quad \Rightarrow \quad \frac{d^2 p_A}{dz^2} - \frac{k_{1,1} RT}{\bar{D}_A^e} p_A p_B = 0$$

Similar to the approach in mass transfer with chemical reaction in a stagnant liquid film (van Krevelen & Hoftijzer, 1948; Hikita & Asai, 1964) the above set of these differential equations can be solved analytically by linearisation of the concentration profiles. If the profile of B is approximated by assuming a constant B concentration over the membrane ( $0 < p_{B,m} \leq p_{B,1}$ ) the reaction is further reduced to a pseudo first order reaction in A, resulting in:

$$\frac{d^2 p_A}{dz^2} - \frac{k'_1 RT}{\bar{D}_A^e} p_A = 0$$

with  $k'_1 = k_{1,1} p_{B,m}$ . Now integration is straightforward and the solutions appear as exponential functions with an eigenvalue  $\phi$ , in fact being the Thiele modulus (see e.g. Westerterp et al., 1983). For the boundary conditions ( $z=0$ ;  $P_A = P(0)$ ) and ( $z=1$ ;  $P_A=0$ ), the solution is:

$$P_A(z) = P(0) \left( \frac{e^{\phi} e^{-\phi \cdot z} - e^{-\phi} e^{\phi \cdot z}}{e^{\phi} - e^{-\phi}} \right) \quad \text{with} \quad \phi = L \sqrt{\frac{k'_1 RT}{\bar{D}_A^e}} \quad (8)$$

Substitution in (6) yields the flux of A as a function of  $z$  in absence of a pressure drop over the membrane. According to Fig. 2, the flux of A at  $z=0$  reaches its maximum value once the slip has reduced to zero, independent whether or not a reaction plane exists. If no contraction or expansion occurs ( $\Delta n=0$ ) the profiles can be linearised (see Fig. 1) and the calculation of the flux at  $z=0$ , provided  $\Delta P=0$ , reduces to the calculation of the diffusive fluxes of A and B to a reaction plane located at  $z=\delta$  ( $0 \leq \delta \leq 1$ ) (Sloot et al., 1991). The reaction stoichiometry of A and B is the additional equation, coupling the fluxes of A and B. For a reaction scheme  $A + \nu_B B = \nu_C C$  (with  $1 + \nu_B = \nu_C$ ), this yields (see Westerterp et al., 1983):

$$N_A = \frac{\bar{D}_A^e}{RT} \cdot \frac{p_A}{L} \left( 1 + \frac{\bar{D}_B^e p_B}{\nu_B \bar{D}_A^e p_A} \right) = N_{ph,max} E_{A,inf} \quad (9)$$

The flux of A at the interface  $z=0$  can be calculated according to eq. (9) in case the slip flux of A ( $N_{A,z=1}$ ) has reduced to zero. This slip flux can be calculated by substituting (8) in (6) for  $z=1$  (B-side). The physical flux ( $N_{A,ph}$ ) can be calculated by integration of (7) for  $k'_1=0$  and substituting the result back in (6). Now a dimensionless relative slip ( $S$ ) can be defined and results in:

$$S = \frac{N_{\text{with reaction, } z=L}}{N_{\text{without reaction, } z=L}} = \frac{N_{A,z=L}}{N_{A,ph}} = \frac{\phi}{\sinh \phi} \quad (10)$$

The approximation results in a simple flux equation (9) and a slip-criterion (10), depending on the kinetics and transport properties of the system. This approximation can be used to evaluate the relative slip of a reactant, without going through the entire modeling.

The accuracy and applicability of the equations (9) and (10) will be experimentally verified in the next paragraphs and the oxidation of carbon monoxide,  $\text{CO} + 0.5\text{O}_2 = \text{CO}_2$ , is taken as a model reaction. In this case a contraction has to be dealt with, but from model simulations it was concluded that eq. (9) is still valid when air was taken as one feedstock and the opposite CO feed was diluted with nitrogen and did not contain over 50% CO.

#### 4. Experimental setup.

A pilot plant of the membrane reactor was constructed consisting of a cylindrically shaped ceramic ( $\alpha$ -alumina) membrane, with in- and outside diameter of 14 mm. and 20 mm. respectively and a length of 275 mm. The important structure parameters are given in Table 2. The membrane was impregnated with platinum which is an active catalyst for most oxidation reactions. Inside the membrane a concentric heat exchanging pipe is placed to remove the heat generated by reaction. The ceramic membrane was sealed to a pair of stainless steel bellows which were connected to the reactor shell. This construction served to account for differences in thermal expansion of the alumina membrane and stainless steel shell. The membrane and its connections were supplied by F. Velterop B.V.. The membrane separates two chambers in which countercurrently the different reactants are supplied, controlled by backpressure regulators. The oxidation of carbon monoxide was taken as a model reaction and a mixture of carbon monoxide and nitrogen was fed to the inner while diluted air (oxygen/nitrogen) was fed to the outer chamber. The complete reactor was placed in an electric oven to compensate for heat loss during reaction and to facilitate starting-up. Thermocouples monitored temperatures at the membrane, the gas phase and the heat transport medium at different locations. Inlet gas feed mixtures of nitrogen/carbon monoxide and nitrogen/air were controlled by mass flow controllers (Brooks). Outlet gas compositions were analysed by an infrared gas analyser ( $\text{CO}_2$ ) (Maihak, UNOR 6N) and a gas chromatograph (Varian 3300).

#### 5. Results and discussion

##### 5.1. Physical flux measurements and parameter estimation

Before starting the conversion experiments the structure parameters ( $B_0$ ,  $K_0$  and  $\epsilon/\tau$ ) of the membrane were determined. From permeation measurements with pure helium and nitrogen the Knudsen parameter,  $K_0$ , and the permeability coefficient,  $B_0$ , were obtained. The  $\epsilon/\tau$ -factor was derived from diffusion experiments of oxygen and carbon monoxide in nitrogen at a temperature of 373 K and at a pressure of 2 Bar.

Continuously supplying one chamber of the membrane with a mixture gas of nitrogen and oxygen or carbon monoxide and the other with pure nitrogen the diffusion fluxes are easily obtained from component mass balances. Based on the solutions to the Graetz problem it was concluded that the results of the flux measurements were not hindered by more than 10% gas transport limitations to the external surface. Therefore interface partial pressures at the external membrane surface were taken to be equal to bulk partial pressures.

From the effective diffusion coefficient as derived from the observed diffusion fluxes  $\epsilon/\tau$  can be calculated from eq. (5b), because the pure gas phase diffusion coefficients are extensively tabled (Reid *et al.*, 1987). The mean pore radius and porosity of the membrane were obtained from mercury penetration. The collected results on the determination of the structure parameters are summarized in Table 2. The pressures at different sides of the membrane could be obtained with an accuracy of 100 Pa, so the diffusion experiments were not affected by convective effects (less than 3%). Measurements of the diffusion coefficients at various temperatures ( $373 \leq T \leq 523$  K) resulted in an Arrhenius temperature dependence of the diffusion coefficients as:

$$D_{\text{O}_2}^e = 0.23 \cdot 10^{-5} \cdot \exp\left(\frac{-260}{T}\right) \text{ m}^2 \cdot \text{s}^{-1} \quad \text{and} \quad D_{\text{CO}}^e = 1.27 \cdot 10^{-5} \cdot \exp\left(\frac{-973}{T}\right) \text{ m}^2 \cdot \text{s}^{-1}$$

##### 5.2 Flux measurements with chemical reaction

According to the theory increasing the membrane activity should increase the flux, until a maximum enhancement is reached meanwhile reducing the slip ( $S$ ) to zero according to eq. (10). In absence of a pressure drop over the membrane, the slip flux of carbon monoxide was measured as a function of increasing reaction rate constant via increasing the membrane temperature. Generally the reaction rate constant depends on temperature according to an Arrhenius expression and so the Thiele modulus (eq. (8)) could be varied. The experimental Thiele modulus was estimated assuming an activation energy of  $5.10^4 \text{ J} \cdot \text{mol}^{-1}$  (Trimm, 1980), while a value for the pre-exponential constant ( $k_0$ ) was fitted matching the initial decrease in slip. The results are shown in Fig. 3 and all experimental points are in good agreement with mass balances as deviations did not exceed 10%.

The general shape of the experimental data band is in reasonable agreement with eq. (10), but obviously shows a steeper slope. Recalculation of the experimental points with an other value of the activation energy, does not yield a substantial better match with the theoretical curve unless unrealistic high values are taken. Changing the value of  $k_0$  only shifts the experimental data in horizontal direction without changing its slope. Most likely the deviation of the curves can be explained by an additional contribution of conversion at the external surface of the membrane in case slip of reactants occurs. The slip calculated according to eq. (10) was derived from a flux model and does not account for a possible additional conversion at the external membrane surface in case a reactant slips through the membrane and penetrates the opposite chamber. Owing to this contribution the observed slip approaches zero at lower values of  $f$ . The conversion of reactants slipped through the membrane cannot be neglected as was learned from premixed feed experiments at 523 K. In excess of oxygen complete conversion of CO at short residence time was obtained. The criterion given by (10) apparently is a worst case for only the conversion in the membrane is taken into account and not at the external surface of the membrane (including dead-end pores), underestimating the total catalytically active area.

If no slip of reactants occurs the fluxes can be calculated according to eq. (9). Figure 4 plots the results. From this

diagram the effective diffusion coefficients of A and B can be obtained from the intercept and slope respectively. When dealing with higher carbon monoxide partial pressures (0.3–0.6 Bar) heat effects became pronounced. Under these conditions the heat generated by reaction was sufficient enough to keep the whole membrane at a temperature of 523 K, while at lower partial pressures additional heating by the electrical oven was necessary. Obviously even when heat effects do become pronounced the fluxes can be estimated with eq. (9). The effective diffusion coefficients from Fig. 4 ( $D_{O_2} = 0.13 \cdot 10^{-5} (\text{m}^2 \cdot \text{s}^{-1})$ ,  $D_{CO} = 0.20 \cdot 10^{-5} (\text{m}^2 \cdot \text{s}^{-1})$ ) agree well (deviations 8% and 0% respectively) with the earlier results for pure diffusion experiments. At higher partial pressures the average temperature was about 530 K, but in this case a temperature gradient over the membrane was observed (30 K). For this reason these data are neglected in the calculation of the effective diffusion coefficients.

The experimental results of the plot of eq. (9) (Fig. 4) support the theoretical work of the previous paragraph. Slood et al. (1990) arrived at the same conclusions under the restrictions of very low partial pressures and a reversible reaction with instantaneous equilibrium. Obviously the expressions (eq. (9)) can be generalised to non-instantaneous reactions and more concentrated systems, provided no slip of reactants occurs (eq. (10)).

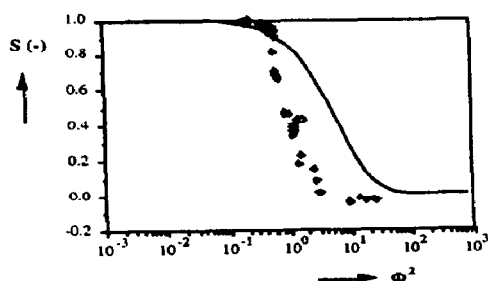


Fig. 3: Slip flux of Carbon Monoxide as a function of the Thiele modulus. Comparison of experimental results ( $\Delta P=0$ ) with eq. 10.

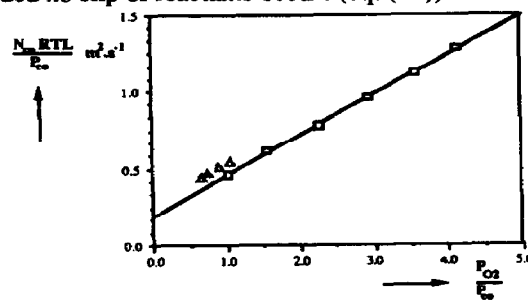


Fig. 4: Plot of eq. 9 at  $T=523 \text{ K}$ . Measurements at low CO pressures (as  $P_{CO} < 0.1 \text{ Bar}$ ) as well as more elevated CO pressures (as  $0.3 < P_{CO} < 0.6$ ). The intercept equals the effective diffusion coefficient of  $O_2$  and the slope is equal to two times the effective diffusion coefficient of oxygen.

### 5.3 Overall conversion measurements

Some explorative conversion experiments have been carried out to test the overall performance of the reactor. Fig. 5 shows the conversion of carbon monoxide as a function of residence time in the inner reactor chamber in absence of a pressure difference over the membrane and at a temperature of 523 K and an absolute pressure of 2.0 Bar. For oxygen in small excess ( $P_{O_2,0} = 0.07 \text{ Bar}$ ,  $P_{CO,0} = 0.1 \text{ Bar}$ ) it clearly demonstrates that high conversion levels, up to 90%, are possible and that over a limited range a linear dependency of conversion on the residence time exists. This linear relationship between the conversion and residence time is a complicated result of increasing  $E_{inf}$  (see (9)) with decreasing carbon monoxide partial pressure. Up to 40% conversion no detectable slip of oxygen and carbon monoxide could be observed. Increasing the residence time and conversion however, led to small amounts ( $< 0.1\%$ ) of oxygen in the CO-chamber. This slip of oxygen again leads to an additional conversion at the external surface, which is probably a second effect leading to the linear dependance of the conversion with residence time. Slip of oxygen could be due to insufficient reaction rate, because decreasing the CO partial pressure (as a result of conversion) shifts the reaction zone to the CO side of the membrane and makes the system more critical towards slip of oxygen. Possibly at high conversions the system becomes also very sensitive to slight inhomogeneous impregnation of the membrane.

## 6. Conclusions

Gas transport inside a membrane can be described with the elaborate Dusty Gas Model, resulting in concentration profiles and fluxes for a variety of boundary conditions and chemical reactions. Solving the set of mass balances inside the membrane with the DGM however is an elaborate task and the calculations are time consuming. The membrane reactor with separated feed of reactants possesses its specific advantages if no reactants slip through the membrane to the opposite side. Therefore for practical application only the fluxes of the reactants at both membrane interfaces are of interest rather than the complete concentration profile over the membrane. In absence of a pressure drop over the membrane a simple flux expression (eq. 12) was derived and a criterion to evaluate whether or not slip of reactants to the opposite side occurs (eq. 14).

In a pilot plant the validity of the flux relations was experimentally tested using the oxidation of carbon monoxide catalysed by a platinum impregnated alumina membrane. From these experiments it was concluded that indeed matching eq. (14) guarantees for no slip of reactants through the membrane and the flux could directly be calculated from eq. (12). Further exploratory experimental work in the pilot plant showed that high conversion levels of carbon monoxide could be obtained.

## 7. Notation

$B_0$  = permeability coefficient ( $\text{m}^2$ )

$D_{i,k}$  = Knudsen diffusion coefficient of component  $i$  ( $\text{m}^2 \cdot \text{s}^{-1}$ )

$E_{act}$  = activation energy ( $\text{J} \cdot \text{mol}^{-1}$ )

$K_0$  = Knudsen coefficient ( $\text{m}$ )

$D_{ij}$  = binary diffusion coefficient of a mixture  $i$  and  $j$  ( $\text{m}^2 \cdot \text{s}^{-1}$ )

$E_{a,inf}$  = maximum enhancement factor (-)

$k_0$  = pre-exponential factor in Arrhenius expres-

$k'_1$  = first order reaction rate coefficient ( $\text{mol.m}^{-3}.\text{Pa}^{-1}.\text{s}^{-1}$ )

$k_{1,1}$  = reaction rate constant of reaction with (1,1)-order  
( $\text{mol.m}^{-3}.\text{Pa}^{-1}.\text{s}^{-1}$ )

$n$  = number of molecules (mol)

$N_{A,z=1}$  = slip flux of A ( $\text{mol.m}^{-2}.\text{s}^{-1}$ )

$N_{A,ph}$  = physical flux of A ( $\text{mol.m}^{-2}.\text{s}^{-1}$ )

$P$  = total pressure (Bar)

$P_{B,m}$  = linearised constant pressure of B in the membrane (Bar)

$R_i$  = reaction rate with respect to component i  
( $\text{mol.m}^{-3}(\text{cat.}).\text{s}^{-1}$ )

$t$  = time (s)

$z$  = space ordinate of integration (m)

$\zeta$  = conversion (-)

$\tau$  = tortuosity (-)

#### Subscripts/superscripts

0 = gas phase

e = effective

ph = physical

i, j, A = component

k = knudsen

sion, units depend on kinetic rate expression

$L$  = membrane thickness (m)

$M_i$  = molecular mass of component i ( $\text{kg.mol}^{-1}$ )

$N$  = flux, relative to a fixed ordinate system  
( $\text{mol.m}^{-2}.\text{s}^{-1}$ )

$N_v$  = viscous flow ( $\text{mol.m}^{-2}.\text{s}^{-1}$ )

$p_i$  = partial pressure of component i (Bar)

$R$  = universal gas constant ( $= 8.314 \text{ J.mol}^{-1}.\text{K}^{-1}$ )

$S$  = relative slip flux at  $z=L$  ( $= N_{A,z=L}/N_{A,ph}$ ) (-)

$T$  = temperature (K)

$x$  = mole fraction (-)

$\phi$  = Thiele modulus (-)

$\epsilon$  = porosity ( $\text{m}^3(\text{gas}).\text{m}^{-3}(\text{cat.})$ )

$\eta$  = membrane efficiency (-)

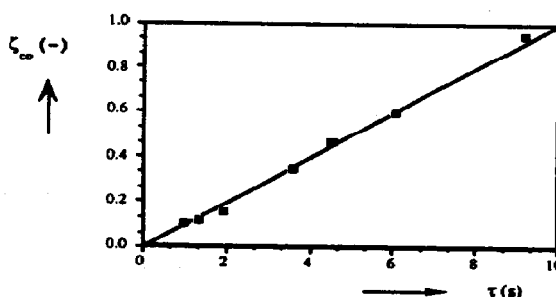


Fig. 5: Conversion of CO as function of residence time observed in the pilot plant. Experimental results at 523 K and 2.0 atm.

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#### Acknowledgements

These investigations were financially supported by the VEG/Gasinstituut, Apeldoorn, the Netherlands. For their contributions in the experimental work, we like to acknowledge K. van Bree, A. Schansem, S. ter Heide, J. Samson and E. Veenendaal. Thanks also to M. Bracht for his contribution in the model calculations.